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## LETTER TO THE EDITOR

# Positron states in fullerites and other carbon phases

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**Abstract.** The positron states and annihilation characteristics are calculated for different phases of carbon: pure and potassium-doped solid  $C_{60}$ , diamond and graphite. In solid  $C_{60}$  with the FCC structure the positron is concentrated in the interstitial space between the  $C_{60}$  molecules. For the different carbon phases the calculated positron lifetimes reproduce well the experimental results in a wide range from about 100 ps for diamond to 400 ps for fullerite. The effects of interstitial dopants on the positron distribution and lifetime are studied for the solid  $C_{60}$ . Finally, the positron characteristics for the compound  $K_xC_{60}$  are predicted and found to be sensitive to the potassium concentration.

The characterization of the exciting structure and properties of fullerite, solid  $C_{60}$ , a new artificially made phase of carbon [1], has motivated a considerable number of investigations. Recently, positron lifetime measurements have also been employed [2–4], thus far mainly in order to explore the possibilities of the method. In order to understand the results of the positron experiments, theoretical calculations of positron states and annihilation rates are necessary. The most important question is that of the assignment of the observed lifetime component of about 400 ps. This is the only component seen in two of the measurements [2, 3]. The origin of this lifetime is, however, unclear. The possibilities discussed are positron annihilation (i) inside the  $C_{60}$  molecules, (ii) in the interstitial open volume between the  $C_{60}$  molecules in the cubic (FCC, BCC and SC) lattice, and (iii) in the open volumes between different  $C_{60}$  solid grains.

In this letter we report on positron state and annihilation calculations for solid  $C_{60}$ . However, we do not only consider solid  $C_{60}$  but enlarge our view of carbon systems by also calculating the positron characteristics for the more familiar diamond and graphite structures. Moreover, we discuss the behaviour of positrons in solid  $C_{60}$  containing impurities and in compounds made by introducing alkaline metal atoms into the interstitial sites of the solid  $C_{60}$ . Some of the latter systems exhibit superconductivity with high critical temperatures and are therefore of considerable current interest [5, 6].

We calculate the positron states and the annihilation rates by solving the full three-dimensional positron Schrödinger equation [7]. The method requires, as input, the positions of the atoms in the solid. For diamond we use the lattice constant 3.56 Å (bond length 1.54 Å). For graphite the bond length within the closely packed planes is 1.42 Å and the distance between the planes is 3.35 Å. These lattice parameters

correspond to room temperature [8]. The basic building block of solid  $C_{60}$  (see figure 1) is a molecule of 60 carbon atoms making a football cage with the atoms at vertices of twenty hexagons and twelve pentagons. There are two different bond lengths, i.e. 1.40 Å between two hexagons and 1.45 Å between a hexagon and a pentagon [9]. At room temperature the  $C_{60}$  molecules form an FCC lattice with the lattice constant 14.2 Å [10]. We use these lattice parameters and orient the  $C_{60}$  molecules with respect to the FCC lattice in such a way that the  $\langle 100 \rangle$  axis bisects a bond between two hexagons (see figure 1). The point group is then  $T_h$ .

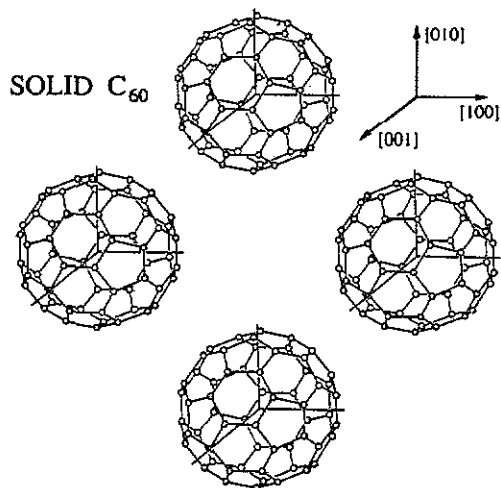


Figure 1. Structure of fullerite. Four  $C_{60}$  molecules belonging to the  $(001)$  plane of the FCC lattice are shown. The carbon atoms are at the vertices of hexagons and pentagons forming the surfaces of the molecules. The interatomic and intermolecular lengths are on the same scale, demonstrating the relatively large open volumes around the octahedral sites between the  $C_{60}$  molecules.

The potential felt by the positron consists of a Coulomb part and a correlation contribution. The latter is treated in the local approximation, i.e. the correlation potential is taken to depend on the local electron density. The Coulomb potential and the electron density for the solid are constructed in this work by superimposing neutral atoms. The positron annihilation rates are calculated within the local density approximation [11] as described in [12]. We use two different models for the electron enhancement at the positron. In the first model (called metallic screening from here on) it is assumed that the screening of the positron at a given point with a certain electron density equals that in a homogeneous electron gas with the same electron density. For simple metals this model gives positron lifetimes that agree well with the measured ones [12]. The great benefit of this model is that it contains no adjustable parameters and therefore the results obtained are true first-principles predictions. In the second model employed (called semiconductor screening from here on) the imperfect screening due to the existence of the electron energy band gap is taken into account [13]. The model is semi-empirical because it uses the measured high-frequency dielectric constant as the input parameter. For semiconductors this model has been shown to give positron lifetimes that agree within a few picoseconds with

experiment [12]. For the insulators with wide band gaps the model gives lifetimes that are somewhat too short. For the dielectric constant we take the value for diamond, i.e.  $\epsilon_{\infty} = 5.66$ , and use it in all cases. This means that the effect of the reduced screening is to decrease the annihilation rate (the inverse of the positron lifetime) approximately by a factor of  $2/\epsilon_{\infty} \text{ ns}^{-1}$  in all systems. Thus the reduced positron screening is considered to be mainly a property of the carbon atom and the bonds to its neighbours and, to a lesser extent, a property of the detailed band structure. The use of non-self-consistent electron structures instead of self-consistent ones has been shown to have small effects on the positron wavefunction and annihilation rate [12].

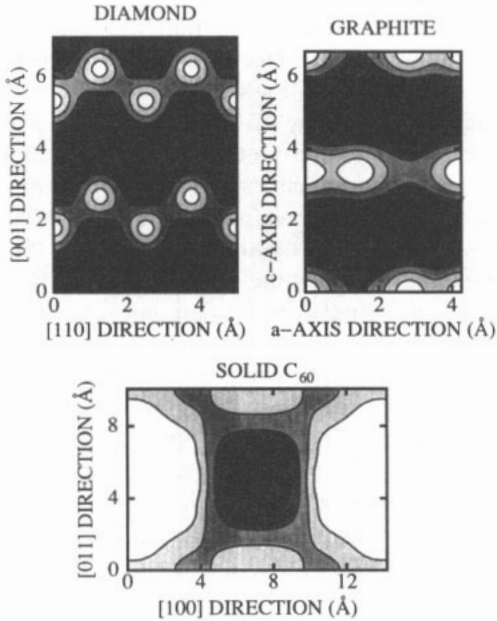
For a proper interpretation of the results obtained by different types of positron annihilation experiments it is essential to know the positron distribution in the crystal lattice. Figure 2 shows the positron wavefunctions in diamond, graphite and solid  $\text{C}_{60}$ . In diamond the positron density is concentrated in the open interstitial space between the atomic chains. However, the density at the bond between two neighbouring atoms is finite, about one fifth of the maximum density. In graphite the positron resides mainly between the close-packed planes. The relative positron density at the carbon bonds is much smaller than at the bonds in the diamond structure. On the other hand, the positron density at the centre of a hexagon is around a quarter of the maximum. In solid  $\text{C}_{60}$  the positron density is concentrated around the octahedral sites of the FCC structure. At the tetrahedral site the density is about one eighth of the maximum. The positron density at the centre of a  $\text{C}_{60}$  molecule is nearly zero. This calculation thus gives a clear negative answer to the question of whether it is possible that the positron resides inside  $\text{C}_{60}$  molecules in fullerite.

Table 1. Positron lifetimes for different pure carbon lattices and for oxygenated and alkali-doped solid  $\text{C}_{60}$  lattices. The positron lifetimes calculated using the metallic ( $\tau^{\text{met}}$ ) and semiconductor ( $\tau^{\text{sc}}$ ) screening models are given. The existing measured positron lifetimes ( $\tau^{\text{exp}}$ ) are shown for comparison.

Lattice	$\tau^{\text{met}}$ (ps)	$\tau^{\text{sc}}$ (ps)	$\tau^{\text{exp}}$ (ps)
Diamond	90	92	110 <sup>a</sup> , 115 <sup>b</sup>
Graphite	180	192	195 <sup>c</sup> , 212 <sup>a</sup>
$\text{C}_{60}$	327	370	396 <sup>a</sup> , 402 <sup>a</sup> , 393 <sup>d</sup> , 403 <sup>e</sup>
$\text{O}_{0.25}\text{C}_{60}$	327	370	
$\text{OC}_{60}$	284	316	
$\text{KC}_{60}$	276	306	
$\text{K}_3\text{C}_{60}$	261	288	
$\text{K}_6\text{C}_{60}$	280	310	

<sup>a</sup> [2]. <sup>b</sup> [14]. <sup>c</sup> [15]. <sup>d</sup> [3]. <sup>e</sup> [4].

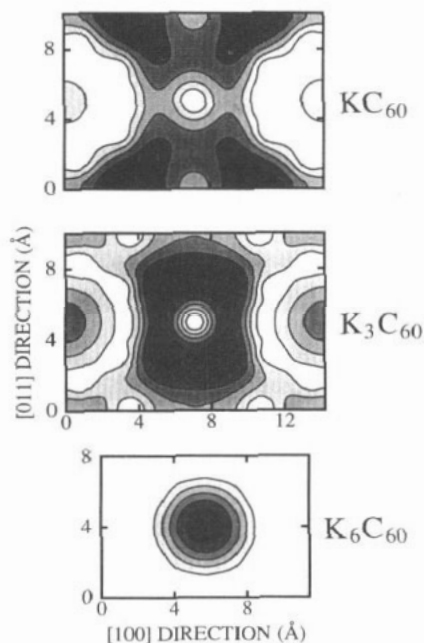
The calculated positron lifetimes for the different carbon phases are given in table 1 and compared with the measured lifetimes. The difference between the theoretical lifetimes for the metallic and semiconductor screening models increases as the lifetime becomes longer. This is because the semiconductor model correction to the annihilation rate is constant. The theoretical values are consistently too low, but the overall trend is surprisingly well reproduced, especially if one takes into account that the positron lifetime increases by a factor of four from diamond to



**Figure 2.** Positron wavefunctions in diamond, graphite and solid  $C_{60}$  lattices. The contour spacing in all parts of the figure is one-sixth of the maximum value in each case. The wavefunction is vanishingly small inside the ion core regions and inside the  $C_{60}$  molecules, which show white in the figure. The darker shading indicates larger values of the wavefunction. In the lowest panel, for solid  $C_{60}$ , the octahedral site is in the centre of the figure and four tetrahedral sites are on the horizontal borders one quarter and three quarters of the side length from the corners.

solid  $C_{60}$ . The relative discrepancy is largest for diamond which is a good insulator, and the enhancement model based on a free-electron gas is not quite adequate [13]. Graphite is a semimetal with a relatively small conduction electron concentration and the semiconductor model for screening seems to work better than for diamond. According to electron structure calculations [16] solid  $C_{60}$  has a direct energy gap of 1.5 eV, and therefore the semiconductor model is expected to be reasonable. This is indeed supported by the fair agreement between theory and experiment seen in table 1, although the actual value of the high-frequency dielectric constant can differ from the value of 5.66 used.

The solid  $C_{60}$  lattice is rather open and soft against external hydrostatic pressure [17]. The softness is due to the fact that the interactions between  $C_{60}$  molecules are weak van der Waals interactions. In contrast, the structure of the  $C_{60}$  molecule is determined by strong covalent interactions and is therefore very stable. In order to interpret the positron lifetime measurements [2] made by varying the external pressure we calculate the positron lifetime as a function of the FCC lattice constant. The atomic structure of the  $C_{60}$  molecules is kept rigid in these calculations. The positron lifetime rises linearly as a function of the lattice constant. The slope around the equilibrium lattice constant is  $56.2 \text{ ps } \text{\AA}^{-1}$ . Schaefer *et al* [2] measured the positron lifetime under a pressure of 3.2 GPa and found a decrease of 24 ps. The dilatation in the lattice constant corresponding to 3.2 GPa is, according to x-ray diffraction measurements



**Figure 3.** Positron wavefunctions in the  $\text{KC}_{60}$ ,  $\text{K}_3\text{C}_{60}$  and  $\text{K}_6\text{C}_{60}$  compounds. The contour spacing in all parts of the figure is one sixth of the maximum value in each case. The wavefunction is vanishingly small inside the ion core regions, which show white in the figure. The darker shading indicates larger values of the wavefunction. Note that for  $\text{K}_6\text{C}_{60}$  (with the BCC lattice) there is a  $\text{C}_{60}$  molecule in the centre of the figure.

[17], about  $0.84 \text{ \AA}$ . The theory then predicts a lifetime decrease of 47 ps, which is larger than the measured one by a factor of two. The use of self-consistent electron densities in the calculations could result in a better agreement with experiment.

The lattice constant of fullerite can also be varied by changing the temperature. At 11 K the lattice constant is found by measurement to be  $14.04 \text{ \AA}$  [18]. According to our theory this lattice constant corresponds to a positron lifetime that is 10 ps shorter than that at room temperature. The actual temperature dependence of the structure of fullerite is, however, more complicated than a simple thermal expansion. Firstly, solid  $\text{C}_{60}$  has a phase transition at 249 K from the FCC structure to a SC structure with a four-atom basis [18]. There is no volume change at the critical temperature but the orientations of  $\text{C}_{60}$  molecules relative to each other change. Owing to the lack of volume change the positron lifetime is not sensitive to this phase transition. We have confirmed the insensitivity by rotating the  $\text{C}_{60}$  molecules relative to each other: the changes in the positron lifetime are less than 1 ps. Another fact to be noted is that both molecular dynamics simulations [19] and NMR experiments [20] indicate that at high temperatures the  $\text{C}_{60}$  molecules rotate quite freely at their lattice sites. Moreover, at high temperatures two different bond lengths cannot be distinguished, but the bond lengths are distributed around  $1.42 \text{ \AA}$  [19], and it is explained that the vibrations of the atoms at finite temperatures wash out the small difference in bond lengths. We have calculated the positron lifetime using the value  $1.42 \text{ \AA}$  for all intermolecular bonds and the room temperature lattice constant  $14.2 \text{ \AA}$ . The

positron lifetime increases by 3 ps from the value obtained by using the bond lengths of 1.40 Å and 1.45 Å. Thus vibrational motions of the atoms on the surface of the  $C_{60}$  molecules are much less important than the change in the lattice constant.

The effects of interstitial oxygen atoms on positron states and annihilation characteristics in solid  $C_{60}$  have also been studied. The resulting lifetimes are given in table 1. When the octahedral sites are only partly occupied—for example, there is an oxygen atom in the middle of every fourth octahedral lattice site ( $O_{0.25}C_{60}$ )—the positron avoids the sites with oxygen and the positron density largely moves to the neighbouring empty sites. As a result, the positron lifetime is almost unaffected. When all the octahedral sites are occupied the positron density has a hole at the centre of each octahedral site. However, the positron density inside the  $C_{60}$  molecules is still much less than in the interstitial regions. The positron lifetime calculated in the semiconductor model has now decreased to the value 316 ps. The effect of other light interstitial impurities on the positron state and lifetime is expected to be similar to that due to oxygen. For example, carbon is slightly more repulsive for positrons than oxygen because of its larger atomic size. In conclusion, the interstitial impurities in solid  $C_{60}$  can affect the positron lifetime only if their concentration is so high that all the octahedral sites are occupied. Moreover, light interstitials prefer to sit at a certain bond distance from the carbon atoms belonging to a  $C_{60}$  molecule rather than at the centre of the octahedral site, leaving even more open space and having less effect than predicted by the calculation.

Alkali metals form compounds with  $C_{60}$  molecules, where the rigid  $C_{60}$  molecules play a role similar to single atoms in usual compounds. These compounds have attracted much interest because some of them are superconducting with relatively high critical temperatures [5, 6].  $K_3C_{60}$  has been found to make a transition to the superconducting state at 19 K, whereas for the heavily doped  $K_6C_{60}$  the transition has not been seen [6]. In  $K_3C_{60}$  the  $C_{60}$  molecules form a FCC lattice and the K atoms occupy all the octahedral and tetrahedral sites. The lattice constant of  $K_3C_{60}$  is 14.24 Å [6], nearly the same as that for pure fullerite.  $K_6C_{60}$  has a BCC lattice with lattice constant 11.39 Å and the K atoms reside near the tetrahedral sites [21].

The positron characteristics for  $K_xC_{60}$  with  $x = 1, 3$  and 6 are predicted. In these calculations we also use the electronic structures of *neutral* atoms although recent first-principles calculations [22] indicate charge transfer from potassium atoms to  $C_{60}$  molecules. The use of more appropriate electron structures for the compounds is expected to decrease the positron density around the potassium atoms with respect to the present results. The calculated positron wavefunction for  $K_3C_{60}$  is shown in the middle panel of figure 3. When the interstitial space becomes filled by K atoms the positron density also penetrates into the  $C_{60}$  molecules. The positron density at the centre of the  $C_{60}$  molecules is close to its global maximum, which occurs near the K atom at the octahedral site. The change in the positron distribution is clearly reflected in the positron lifetime: in the semiconductor model it decreases to the value 288 ps. In the case of  $K_6C_{60}$  the positron density is shifted inside the  $C_{60}$  molecules as shown in the lowest panel of figure 3. The positron lifetime has now increased to the value 310 ps. The compound  $KC_{60}$ , in which only the octahedral sites of the FCC  $C_{60}$  lattice are occupied, is also considered. In this compound the positron density peaks around the tetrahedral interstitial sites as shown in the uppermost panel of figure 3 and the positron lifetime has the value 306 ps.

For the positron lifetime in  $K_xC_{60}$  compounds the calculations predict an interesting non-monotonic behaviour as a function of the potassium concentration. We

therefore suggest making positron lifetime measurements as a function of potassium exposure in a fashion similar to recent photoemission measurements [23]. The predicted change in the environment where the positron annihilates is also likely to influence the angular correlation of the annihilating positron-electron pair. The situation is to some extent analogous to positron annihilation in graphite intercalation compounds [24]. In pure graphite the angular correlation curves show features characteristic for bonds between carbon atoms. When graphite is intercalated with potassium, the angular correlation data resemble those for metallic potassium. In the case of  $K_xC_{60}$  compounds the potassium signal is predicted first to appear and then to disappear as a function of potassium exposure.

In conclusion, we have calculated the positron states and lifetimes for different carbon structures. In fullerite the positron density is concentrated in the open interstitial sites between the  $C_{60}$  molecules. The positron lifetime calculated for this state is slightly less than 400 ps, in good agreement with the component seen in the experimental lifetime spectra. The addition of a small concentration of dopants does not affect the positron lifetime. The positron is in a highly delocalized state in solid  $C_{60}$  and can therefore find unoccupied interstitial sites. Only when all the interstitial sites are occupied is the positron density shifted strongly toward the centres of the  $C_{60}$  molecules, and then the positron lifetime decreases. This is predicted to happen, for example, for the superconducting  $K_3C_{60}$  compound. Finally, when the interstitial space between the  $C_{60}$  molecules is filled by foreign atoms, as in the case of BCC  $K_6C_{60}$ , the positron density resides inside the  $C_{60}$  molecules.

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